Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Synthesis of *α*-biotinyl poly(ethylene glycol-*b*-*N*-isopropylacrylamide) block copolymers with different fluorescent dyes at the *ω*-side

*Wolfgang Birnbaum, Dirk Kuckling**

Department Chemie, Universität Paderborn, Warburger Str. 100, D-33098 Paderborn, Germany

Table S1 Experimental data of the synthesis of biotinylated PNIPAAm in DMSO:

entry	NIPAAm	initiator	CuCl	$CuCl_2$	Me_6TREN	DMSO
A1	2.175 g, 19.22 mmol	**3**, 28.0 mg, 0.07 mmol	10.40 mg, 0.11 mmol	3.6 mg, 0.03 mmol	37 µl, 0.13 mmol	4.8 mL
A2	2.175 g, 19.22 mmol	**3**, 10.8 mg, 0.03 mmol	4.1 mg, 0.04 mmol	1.4 mg, 0.01 mmol	14 µl, 0.05 mmol	4.8 mL
A3	2.175 g, 19.22 mmol	**3**, 81.1 mg, 0.19 mmol	31.5 mg, 0.32 mmol	10.3 mg, 0.08 mmol	113 µl, 0.38 mmol	4.8 mL
A4	2.178 g, 19.25 mmol	**3**, 20.3 mg, 0.05 mmol	7.7 mg, 0.08 mmol	2.4 mg, 0.02 mmol	28 µl, 0.10 mmol	4.8 mL
A5	2.175 g, 19.22 mmol	**3**, 13.5 mg, 0.03 mmol	5.1 mg, 0.05 mmol	1.8 mg, 0.01 mmol	19 µl, 0.06 mmol	4.8 mL
B1	1.813 g, 16.02 mmol	**6**, 73.2 mg, 0.11 mmol	17.0 mg, 0.17 mmol	5.7 mg, 0.04 mmol	62 µl, 0.21 mmol	5.3 mL
B2	1.631 g, 14.41 mmol	**6**, 36.6 mg, 0.05 mmol	8.5 mg, 0.09 mmol	2.9 mg, 0.02 mmol	31 µl, 0.11 mmol	4.8 mL
B3	3.142 g, 27.77 mmol	**6**, 36.6 mg, 0.05 mmol	8.5 mg, 0.09 mmol	2.9 mg, 0.02 mmol	31 µl, 0.11 mmol	9.2 mL
C1	0.680 g, 6.01 mmol	**9**, 92.3 mg, 0.03 mmol	4.2 mg, 0.04 mmol	1.4 mg, 0.01 mmol	16 µl, 0.05 mmol	2.0 mL
C2	1.360 g, 12.02 mmol	**9**, 92.3 mg, 0.03 mmol	4.2 mg, 0.04 mmol	1.4 mg, 0.01 mmol	16 µl, 0.05 mmol	4.0 mL
C3	2.719 g, 24.03 mmol	**9**, 92.3 mg, 0.03 mmol	4.2 mg, 0.04 mmol	1.4 mg, 0.01 mmol	16 µl, 0.05 mmol	8.0 mL

Table S2 Experimental data of the synthesis of α-biotinyl-PNIPAAm with ω-dye-functionalization by sequential monomer addition:

entry	NIPAAm	initiator	CuCl	$CuCl_2$	Me_6TREN	dye	solvent
D1	1.333 g, 11.78 mmol	**3**, 24.9 mg, 0.06 mmol	9.3 mg, 0.09 mmol	3.2 mg, 0.02 mmol	35 µl, 0.12 mmol	**12**, 136 mg, 0.24 mmol	DMSO, 3.9 mL
D2	1.333 g, 11.78 mmol	**3**, 24.9 mg, 0.06 mmol	9.3 mg, 0.09 mmol	3.2 mg, 0.02 mmol	35 µl, 0.12 mmol	**10**, 95 mg, 0.24 mmol	DMSO, 3.9 mL
D3	1.333 g, 11.78 mmol	**3**, 24.9 mg, 0.06 mmol	9.3 mg, 0.09 mmol	3.2 mg, 0.02 mmol	35 µl, 0.12 mmol	**14**, 71 mg, 0.24 mmol	DMSO, 3.9 mL
E1	0.667 g, 5.89 mmol	**6**, 20.2 mg, 0.03 mmol	4.7 mg, 0.05 mmol	1.6 mg, 0.01 mmol	17 µl, 0.06 mmol	**12**, 136 mg, 0.24 mmol	DMSO, 2.0 mL
E2	0.667 g, 5.89 mmol	**6**, 20.2 mg, 0.03 mmol	4.7 mg, 0.05 mmol	1.6 mg, 0.01 mmol	17 µl, 0.06 mmol	**10**, 95 mg, 0.24 mmol	DMSO, 2.0 mL
E3	0.667 g, 5.89 mmol	**6**, 20.2 mg, 0.03 mmol	4.7 mg, 0.05 mmol	1.6 mg, 0.01 mmol	17 µl, 0.06 mmol	**14**, 71 mg, 0.24 mmol	DMSO, 2.0 mL
E4	1.066 g, 9.42 mmol	**6**, 32.2 mg, 0.05 mmol	9.3 mg, 0.09 mmol	-	28 µl, 0.10 mmol	**12**, 109 mg, 0.19 mmol	DMF/H_2O, 4.9 mL
E5	1.066 g, 9.42 mmol	**6**, 32.2 mg, 0.05 mmol	9.3 mg, 0.09 mmol	-	28 µl, 0.10 mmol	**10**, 76 mg, 0.19 mmol	DMF/H_2O, 4.9 mL
E6	1.066 g, 9.42 mmol	**6**, 32.2 mg, 0.05 mmol	9.3 mg, 0.09 mmol	-	28 µl, 0.10 mmol	**14**, 57 mg, 0.19 mmol	DMF/H_2O, 4.9 mL

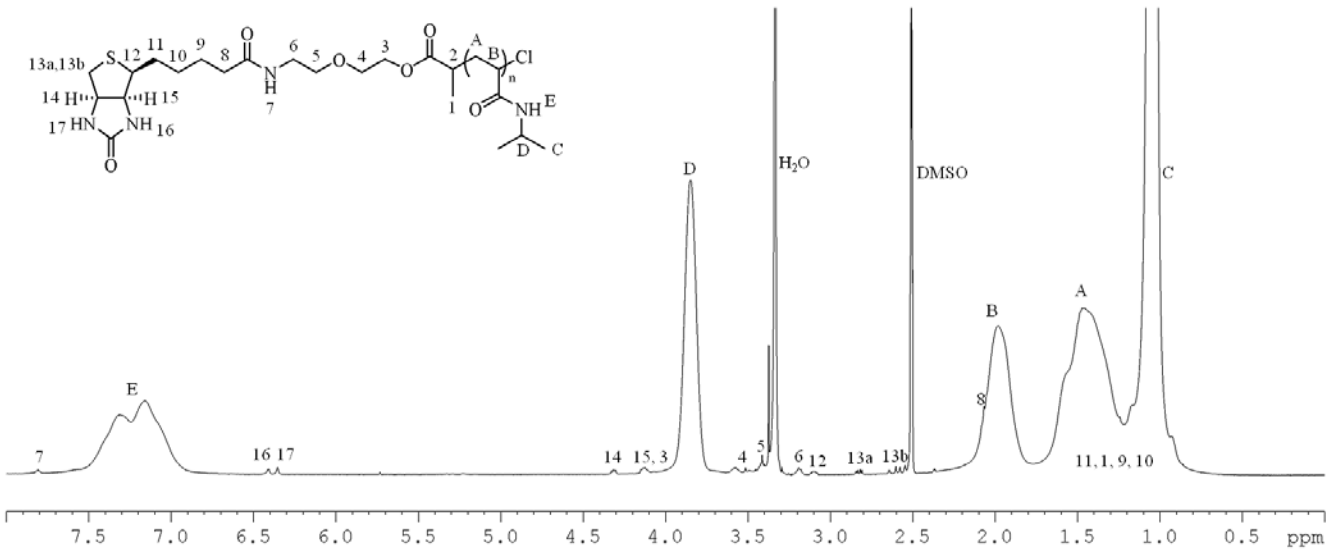
Table S3 Experimental data of the preparation of azide terminated PNIPAAm:

entry	starting material	NaN_3	DMF
F1A	**F1**, 0.35 g	56.9 mg, 0.88 mmol	1.5 mL
F2A	**F2**, 0.85 g	115 mg, 1.77 mmol	3.5 mL
F3A	**F3**, 1.60 g	100 mg, 1.54 mmol	6.6 mL

Table S4 Experimental data of dye functionalization via click reaction (CuAAC):

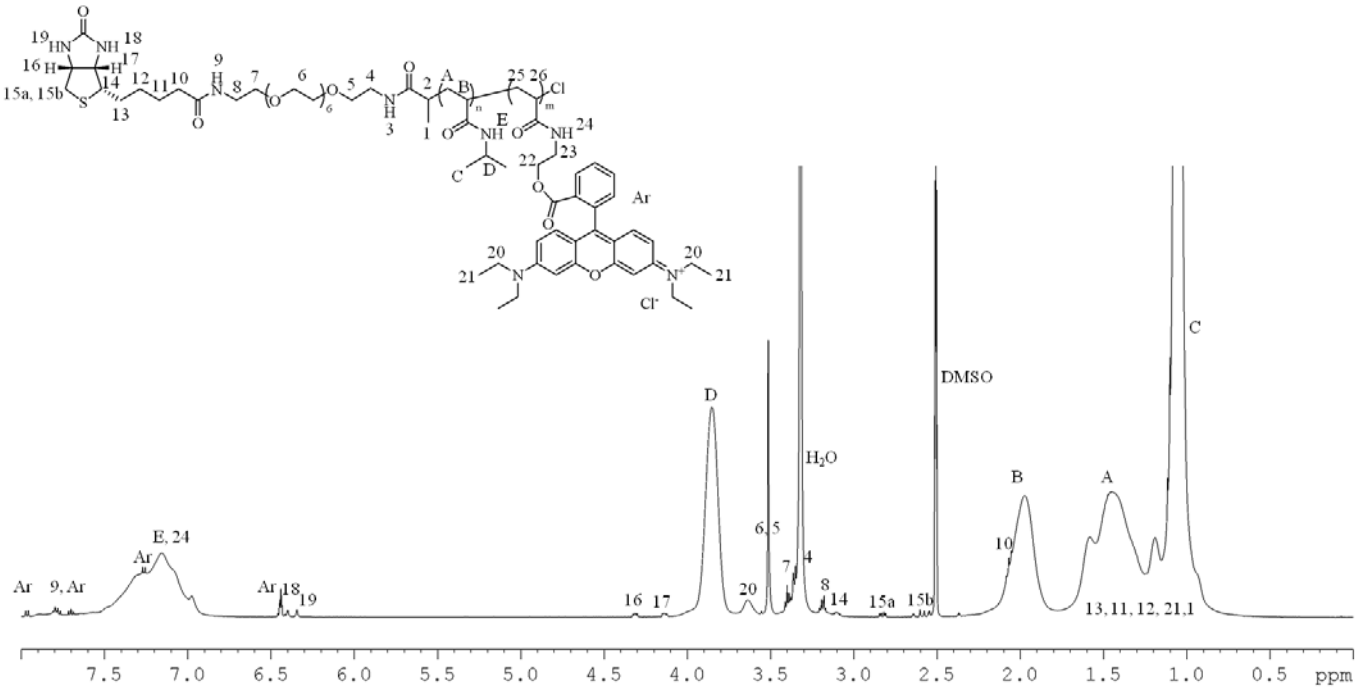
entry	starting material	CuBr	PMDETA	dye	DMF
F1RhB	**F1A**, 0.200 g	7.2 mg, 0.05 mmol	20.7 µl, 0.10 mmol	**13**, 26.7 mg, 0.05 mmol	3 mL
F2RhB	**F2A**, 0.200 g	6.0 mg, 0.04 mmol	17.4 µl, 0.08 mmol	**13**, 21.5 mg, 0.04 mmol	3 mL
F2Flu	**F2A**, 0.200 g	6.0 mg, 0.04 mmol	17.4 µl, 0.08 mmol	**11**, 15.4 mg, 0.04 mmol	3 mL
F2Cou	**F2A**, 0.200 g	6.0 mg, 0.04 mmol	17.4 µl, 0.08 mmol	**15**, 8.9 mg, 0.04 mmol	3 mL
F3RhB	**F3A**, 0.400 g	5.5 mg, 0.04 mmol	16.0 µl, 0.08 mmol	**13**, 19.9 mg, 0.04 mmol	3 mL
F3Flu	**F3A**, 0.400 g	5.5 mg, 0.04 mmol	16.0 µl, 0.08 mmol	**11**, 14.2 mg, 0.04 mmol	3 mL
F3Cou	**F3A**, 0.400 g	5.5 mg, 0.04 mmol	16.0 µl, 0.08 mmol	**15**, 8.2 mg, 0.04 mmol	3 mL

Fig. S1 Sample ^{1}H NMR spectra of polymer **A1** and calculation of the molecular weight of the PNIPAAm block



$$\mathrm{MW(PNIPAAm)} = \frac{\mathrm{integral(H_D)}}{\frac{\mathrm{sum\ of\ integrals(H_{16} + H_{17} + H_{13a})}}{3}} \cdot \mathrm{M(NIPAAm)}$$

Fig. S2 Sample ^{1}H NMR spectra of polymer **E4** and calculation of the molecular weight of the PNIPAAm block and degree of dye functionalization



$$\mathrm{MW(PNIPAAm)} = \frac{\mathrm{integral(H_D)}}{\frac{\mathrm{sum\ of\ integrals(H_6 + H_5)}}{26}} \cdot \mathrm{M(NIPAAm)}$$

$$\text{Degree of dye functionalization} = \frac{\frac{\text{integral}(H_{20})}{8}}{\frac{\text{sum of integrals}(H_6 + H_5)}{26}}$$

Fig. S3 UV-Vis spectra of propargylated rhodamin B **13**, rhodamin B monomer **12**, polymer **E4** and polymer **F2RhB**, all showing an absorption maxima at 563 nm.